

Hydrogen influence on generalized stacking fault of Zr {0001} plane: a first-principles calculation study

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Abstract

The influences of hydrogen on the generalized stacking fault (GSF) energies of the basal plane along the $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions in hcp Zr were investigated using the first-principles calculation method. The modifications of the GSF energies were studied with respect to the different distances of H atoms away from the slip plane and hydrogen content there. The calculation results have shown that the GSF energies along the $\langle 10\bar{1}0 \rangle$ direction drastically reduce when H atoms locate nearby the slip plane. But H atoms slightly decrease the GSF barrier for the $\langle 11\bar{2}0 \rangle$ slipping case. Meanwhile, with the increase of hydrogen density around the slip plane, the GSF energies along both the two shift directions further reduced greatly. The physical origin of the reduction of GSF energies due to the existence of hydrogen atoms in Zr was analyzed based on the Bader charge method. It is interpreted by the Coulomb repulsion of the Zr atoms beside the slip plane due to the charge transfers from Zr to H.

Keywords: First principles, hydrogen, Zirconium, stacking fault energy,

1. Introduction

The generalized stacking fault (GSF), as discussed by Vitek[1], is often correlated with the dislocations mobility and plasticity of materials. The mechanical properties of metal materials are primarily affected by the mobility of dislocations. By modulating the GSF energy profile with the introduction of different element atoms, the recent works by Pei et al. [2, 3] have reported the improvement of the mechanical properties of metals (such as Mg, Al). Hexagonal close-packed (hcp) zirconium and its alloys are used widely as structural materials in nuclear reactors due to their low neutron absorption cross section, good mechanical properties and superior corrosion resistance [4]. Particularly, they are used as the cladding materials in light water nuclear reactors. The effects of H atoms in Zr and its alloys are a long term issue with respect to the reduction of their mechanical performances. The earlier works announced that the addition of H atoms would drastically decrease the GSF energy of the typical slip planes (primary basal plane and prismatic plane) in hcp Zr [5, 6, 7]. But the later literature by Udagawa et al. [8] explained the main reason of hydrogen embrittlement of Zr alloys to be the brittle nature of the hydride rather than the solid solution of Zr-H system.

Recently, Wu et al.[9] proposed a interpretation for the GSF features of different pure hcp metals based on the correlation of GSF and the unit cell volume as well as the ratio of lattice constant (c/a). Shang et al. [10] tried to explain the physical mechanism of the GSF modification caused by alloying

with other elements in hcp Mg by employing the analysis method of differential charge density. However, it is still unclear how H atoms interact with Zr atoms beside the slip planes, and the physical reasons of the reduction of the GSF energies in hcp Zr containing H atoms. The purpose of this work is to systematically investigate the interaction of H atoms and the stacking faults in hcp Zr. The dependences of $1/3\langle 10\bar{1}0 \rangle\{0001\}$ and $1/3\langle 11\bar{2}0 \rangle\{0001\}$ GSF energy profiles on the distance between H atoms and the slip plane as well as the H concentration are calculated based on the density functional theory (DFT) method. Meanwhile, the Bader charge in combination with the structural features are adapted to explore the physical origin of reduction of GSF energy caused by H atoms neighboring the slip plane along two shift directions. The results demonstrate that the Coulomb interactions between positively charged Zr atoms beside the slip planes cause the decrease of energy barrier of $1/3\langle 10\bar{1}0 \rangle\{0001\}$ GSF structure, whereas for $1/3\langle 11\bar{2}0 \rangle\{0001\}$ GSF structure, the wide atomic space of $\{0001\}$ planes weakens the Coulomb repulsion, and the energy barrier for the atomic plane shifting would be affected slightly. But as the increase of H concentration around the slip region, the enhanced Coulomb interaction between the slipping planes obviously reduces GSF energies of both GSF structures. Accordingly, the calculation method and model is given in Section II, followed by the results and discussions including DFT calculation and Bader charge analysis. The conclusions will be presented finally.

2. Methods and Model

2.1. Computational method

Our DFT calculations were performed using the projector augmented wave (PAW) [11] as implemented in the Vienna ab initio simulation package (VASP) [12]. The Perdew-Burke-Ernzerhof (PBE) [13] scheme of the generalized gradient approximation (GGA) is adapted to describe exchange and correlation. To get accurate results, the plane wave cut-off energy is chosen as 400 eV for all calculation. The Brillouin zone sampling employs the γ -centered grids of kpoints of $11 \times 11 \times 1$ in terms of Monkhorst-Pack scheme [14]. The quasi-Newton algorithm was used to relax the ions until the energy and the Hellmann-Feynman force was less than 10^{-4} eV and 0.05 eV/Å.

2.2. Theoretical model

The volume and atom position are allowed to fully relaxed to obtain the lattice parameter of single hcp zirconium. Our calculated results ($a = 3.235$ Å, $c/a = 1.604$) agrees well with experimental [16] ($a = 3.23$ Å, $c/a = 1.594$) and other theoretical results[8]. Hydrogen as a small atom will locate tetrahedron or octahedron interstitial position when it gets into the hcp zirconium system. A $3 \times 3 \times 2$ supercell containing 36 Zr atoms and 1 H atom was constructed to investigate which position H atom locate is stable. The total energy difference (denoted as $E(T)-E(O)$) between these two configurations we calculated is -0.052 eV, which is in good agreement with other theoretical observations (-0.057 eV [6], -0.061 eV [17]), indicating T-site is stable. Consequently, the model we adapted in this work was constructed with H atom in tetrahedron interstitial position. As illustrated in Fig. 1, a $1 \times 1 \times$

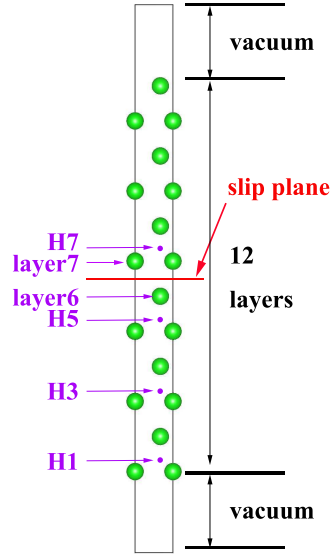


Figure 1: The model of hcp Zr with H atom locating different position represented by VESTA[15]. Zr: big green spheres; H: small purple spheres. H1, H3, H5 stand for pure 12 layers hcp Zr with one H atom locating in the tetrahedron above layer1, layer3, layer5 separately. H57 presents that two H atoms are putted into two tetrahedrons above layer5 and layer7 simultaneously.

12 supercell with 8 Å vacuum between them are constructed to prevent any interactions between periodic images for calculating GSF energy curves. The stable interstitial position is T-site when a hydrogen atom is added to hcp zirconium system. We named layer1, layer2, ..., layer12 from the bottom to the top of the hcp zirconium supercell. We called the structure as H1, H3, H5 separately, when we put a hydrogen atom in a tetrahedron above layer1, layer3, layer5. That is, the hydrogen is the closest to the slip plane in H5. Meanwhile, we place two hydrogen atoms in two tetrahedrons above layer5 and layer7 separately to study the influences of the hydrogen concentration on the GSF energy, which is denoted as H57.

3. Results and discussion

3.1. GSF energy of basal plane

Fig.2 presents the GSF energy curves of $\{0001\}$ along $\langle 10\bar{1}0 \rangle$ as a function of fractional displacement for pure Zr and the Zr-H system. For the pure Zr, the maximum value (about 0.276 J/m²) as well as the fault position it reached (at 7/10, 8/10 of total displacement) agree well with previous results (about 0.275 J/m²)[8], confirming the reliability of our calculations.

Fig.2 shows the remote H atom from the slip plane (H1,H3) slightly decrease the GSF energy curves of the hcp Zr, while the nearest H atom (H5) drastically decrease the GSF energy curve. In the H5 case, the γ_{US} (unstable stacking energy) and γ_{SF} (stacking fault energy) are predicted to decline from 0.276 J/m² and 0.228 J/m² to 0.152 J/m² and 0.039 J/m² (nearly 45% and 83%) due to the addition of the H atom nearest to the slip plane. According to the study of Wu et al.[9], the structural properties are important

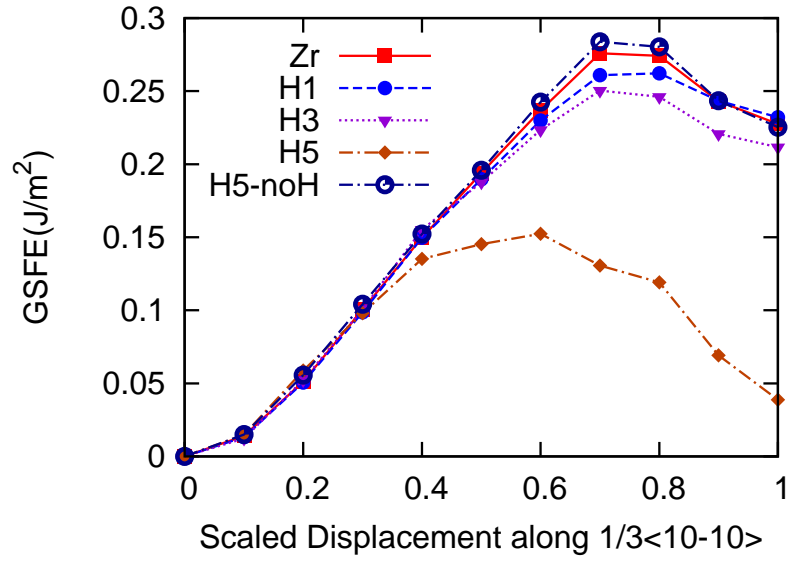


Figure 2: The GSF energy curves of pure Zr and Zr-H system with H atom locating different position versus fractional displacement along $\langle 10\bar{1}0 \rangle$ direction in the basal plane

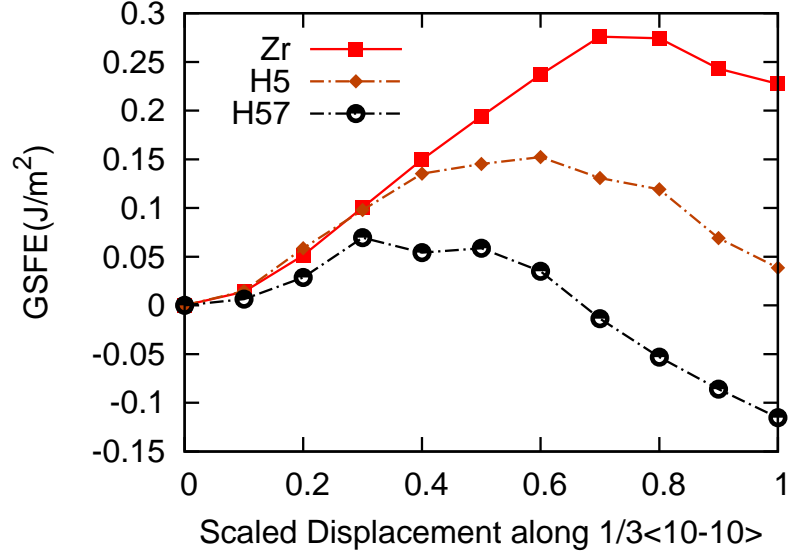


Figure 3: The GSF energy curves of pure Zr and Zr-H system with different concentration of H atom versus fractional displacement along $\langle 10\bar{1}0 \rangle$ direction in the basal plane

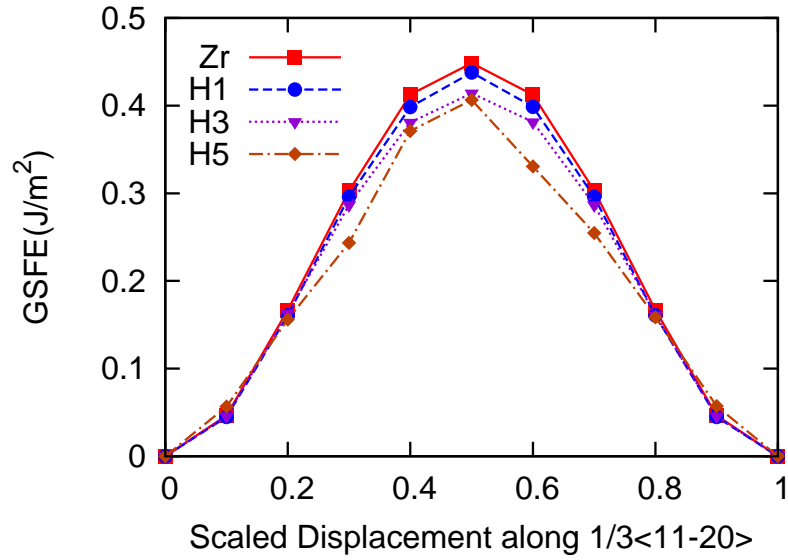


Figure 4: GSF energy curves versus fractional displacement along $\langle 11\bar{2}0 \rangle$ direction in the basal plane

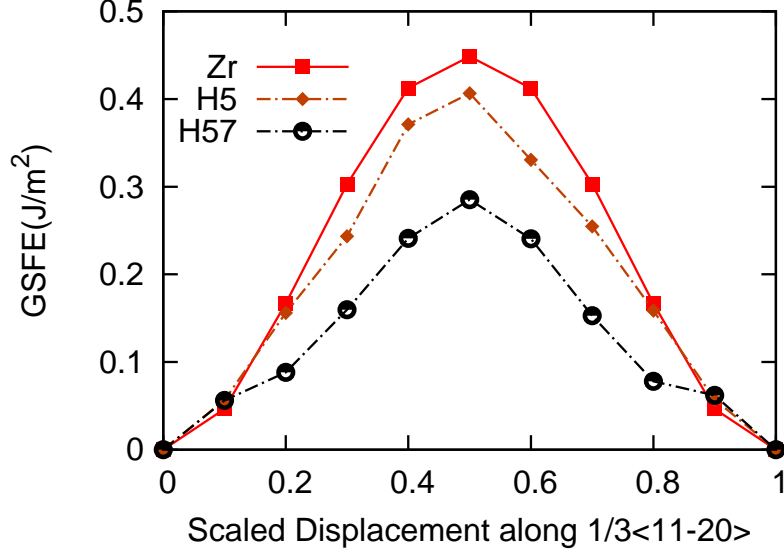


Figure 5: The GSF energy curves of pure Zr and Zr-H system with different concentration of H atom versus fractional displacement along $\langle 11\bar{2}0 \rangle$ direction in the basal plane

factors that influence the GSF energy curves for pure metals. Therefore, we suppose the dramatically change of GSF energy curve is because of volume expansion. So we remove the H atom from the relaxed H5 case to study the effect of volume expansion on the GSF energy curve, and the result is shown as H5-noH in Fig.2. However, It is found that the γ_{US} is slightly increased because layer6 and layer7 are closer due to the squeezing force of H atom to its neighboring Zr atoms. So structural characters are not enough to fully understand the trends of GSF energy curve after adding a H atom.

In order to further study the effects of the hydrogen concentration on the GSF energy curve, we calculated the GSF energy curve of H57, which is plotted in Fig. 3 as well as the ones of Zr and H5. It is clearly found that the γ_{US} was rapidly reduced to 0.070 J/m² for H57 from 0.152 J/m² for H5

after the addition of one more H atom. Meanwhile, the γ_{SF} of H5 dropped from 0.039 J/m² to -0.115 J/m² for H57. It means that the stable stack fault of H57 structure is more stable than the unchanged one.

Table 1: Influence of H on the GSF energy curve (J/m²) in Zr for the basal plane

	$\gamma_{US} < 10\bar{1}0 >$	$\gamma_{SF} < 10\bar{1}0 >$	$\gamma_{US} < 11\bar{2}0 >$
pure Zr	0.276	0.227	0.449
H1	0.262	0.232	0.438
H3	0.250	0.212	0.414
H5	0.152	0.039	0.407
H57	0.070	-0.115	0.285

Similar to Fig.2 and Fig.3, we plotted out the results along $< 11\bar{2}0 >$ of $\{0001\}$ in Fig.4 and Fig.5, which is another common slip pattern in basal plane for hcp metals. Like the results along $< 11\bar{2}0 >$, the γ_{US} is becoming smaller as the H atom closer to the slip plane or increasing the content of H atom. The details are shown in Table. 1.

However, it is observed that the magnitude of decline along $< 11\bar{2}0 >$ direction is much smaller than that along $< 10\bar{1}0 >$ direction for the structures containing one H atom. For the case of H5, the γ_{US} along $< 11\bar{2}0 >$ is merely 0.042 J/m² smaller than the γ_{US} in pure Zr. The reasons behind this will be discussed carefully in next section considering both structural and electronic properties.

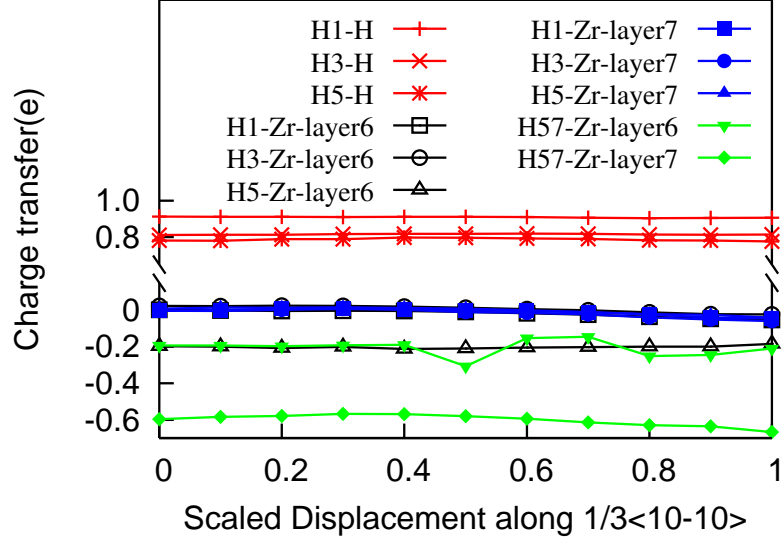


Figure 6: The bader charges transfer of H and Zr atom of layer6 and layer7 in H1, H3, H5, H57 structure versus fractional displacement along $\langle 10\bar{1}0 \rangle$ direction in the basal plane. The positive values present obtaining electrons while the negative ones mean losing electrons.

Table 2: The numbers of charge transfer caused by H, C, N in H5 structre. The positive values present obtaining electrons while the negative ones mean losing electrons.

Charge transfer(e)	Zr ₁₂ H	Zr ₁₂ C	Zr ₁₂ N
solute atom	0.79	1.77	1.71
Zr(layer6)	-0.21	-0.49	-0.48

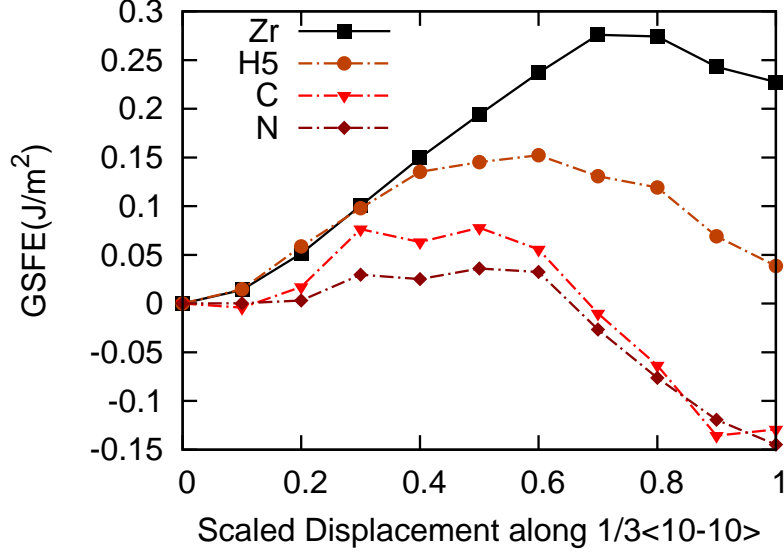


Figure 7: The effect of addition of H, C, N on the GSF energies in H5 structure versus fractional displacement along $\langle 10\bar{1}0 \rangle$ direction in the basal plane

3.2. Bader charge analyse

It's natural to understand the change of γ_{US} in the view of charge properties. Actually, in a recently work[10], the authors attribute the variations of γ_{US} caused by the adding of alloy elements to the redistribution of charge density of Mg-based alloys. As for our case, we calculated the charge transfers of each atom caused by the addition of H atom along $\langle 10\bar{1}0 \rangle$ in terms of Bader charge analysis[18, 19], which are presented in Fig. 4 as a function of displacement. It is found that: (1) the H atom obtain electrons showing stronger electronegativity while the Zr atom lose electrons. (2) the values of charge transfer for both H and Zr in H1, H3, H5, H57 structures remain nearly unchanged in the whole shift process. (3) the charge transfers of Zr in layer6 are almost zero due to being far away from the H atom in H1, H3

structures, while in the H5 and H57 cases, the Zr atom in layer6 lose about 0.2 electrons. Furthermore, the Zr atom in layer7 of H57 lose as many as about 0.6 electrons.

There will be a repulsive force between two atoms with the same kind of charge. Therefore it is natural to propose that the Coulomb repulsion is the reason behind the decline phenomenons of GSF energy curves caused by H atom in hcp Zr. The Coulomb repulsion between the Zr atoms in layer6 and layer7 will become stronger due to the increase of charges of Zr in layer6. The relationship is more obvious for the H57 case, where the γ_{US} is further reduced compared to the H5 case because of more charge transfers for Zr atoms in layer7.

That is to say, there maybe a direct relationship between the magnitude of decline and the amount of charge transfer caused by the H atom. In order to test and clarify the rationality of our hypothesis, we replaced H atom by C, N separately in H5 structure, and then their GSF energy curves along $\langle 10\bar{1}0 \rangle$ and charge transfers were calculated, obtained results shown in Fig. 7 and Table.2.

From Fig.7, We find that the magnitudes of decline induced by C, N are much bigger than the ones caused by H, consistent with the results that the charge transfers caused by C, N are much more than the ones caused by H, as shown in Table 2. Furthermore, it is reasonable to conclude that the similar GSF energy curves of Zr-C, Zr-N system result from the nearly same charge transfers caused by C, N separately. As a result, our proposal are confirmed directly in basal plane of hcp Zr.

As mentioned in last section, problems are still existed in the results of

GSF energy along $\langle 11\bar{2}0 \rangle$ since the magnitude of decline is much more smaller than that along $\langle 10\bar{1}0 \rangle$. With the H5 structure as an example, it is found that the distance between the layer6 and layer7 along $\langle 11\bar{2}0 \rangle$ is about 0.15 Å larger than the one along $\langle 10\bar{1}0 \rangle$ in relaxed H5 structure. It will result in weakening the influence of the charge transfer on the GSF energy since 0.15 Å is considerable in the atom scale. Maybe the Coulomb repulsion could be negligible when the distance reaches certain value.

Consequently, the phenomenons of decline caused by H atom in hcp Zr are interpreted qualitatively by charge transfers and structure properties.

4. Conclusion

In present work, the GSF energy curves of $\{0001\}$ along $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions for both pure Zr and four Zr-H systems were calculated using Density Functional Theory as implemented in VASP. The effects of distance to the slip plane and concentration of H atom on the GSF energy curves were thoroughly investigated. In order to clarify the reason of the declines of GSF energy curves caused by H atom, the method of Bader charge analysis is adapted. Our results are summarized as follows: (1) The decreasing effect become more obviously as the H atom closer to the slip plane. Specially, in the H5 case along $\langle 10\bar{1}0 \rangle$, the γ_{US} and γ_{SF} are reduced significantly by 45% and 83% separately. (2) The content of H atom is another factor that decrease the GSF energy profile. (3) Using the Bader charge analysis, we find there are more charge transfers in layer6 when the H atom is closer to the slip plane. More charge transfers mean stronger Coulomb repulsion, and that will lead to larger magnitude of decline in GSF energy curves. (4) The

magnitude of decline caused by H atom along $\langle 11\bar{2}0 \rangle$ direction is much smaller than that along $\langle 10\bar{1}0 \rangle$ direction for the structures containing one H atom. Coulomb repulsion will be weakened because the distance between the layer6 and layer7 along $\langle 11\bar{2}0 \rangle$ is about 0.15 Å larger than the one along $\langle 10\bar{1}0 \rangle$ in relaxed H5 structure. Therefore, a less obvious decrease of GSF energy curve (Fig.5) along $\langle 11\bar{2}0 \rangle$ is reasonable. (5) Our conclusions are verified by replacing H with C and N in H5 structure.

This work provides more deeper understandings on the behavior of H in hcp Zr, and the result that the dislocation occur more easier in the part there are more H atoms is predicted, which will be useful for the researchers working in the light water nuclear field.

Acknowledgments

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